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EP 4 303 980 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
10.01.2024 Bulletin 2024/02

(51) International Patent Classification (IPC):
H01M 10/0567 (2010.01) **H01M 10/052** (2010.01)

(21) Application number: **22763475.5**

(52) Cooperative Patent Classification (CPC):
H01M 10/052; H01M 10/0567; Y02E 60/10

(22) Date of filing: **04.02.2022**

(86) International application number:
PCT/KR2022/001751

(87) International publication number:
WO 2022/186490 (09.09.2022 Gazette 2022/36)

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

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(30) Priority: **04.03.2021 KR 20210028511**

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(54) **ELECTROLYTE SOLUTION FOR SECONDARY BATTERY, AND SECONDARY BATTERY
COMPRISING SAME**

(57) The present invention relates to a non-aqueous electrolyte solution for a secondary battery, and a secondary battery comprising same. Adding a compound represented by chemical formula 1 or chemical formula 2 to a non-aqueous electrolyte solution for a secondary

battery according to the present invention has the effect of improving room-temperature and high-temperature thermal stability characteristics, and high-temperature storage characteristics.

Description

[Technical Field]

5 [0001] The present invention relates to an electrolyte solution for a secondary battery and a secondary battery including the same, and more particularly to a non-aqueous electrolyte solution for a secondary battery and a secondary battery including the same, in which a compound of Chemical Formula 1 or Chemical Formula 2 is added to a non-aqueous electrolyte solution for a lithium ion secondary battery, thereby effectively increasing the stability of the non-aqueous electrolyte solution.

10 [Background Art]

15 [0002] Recently, portable electronic devices have been widely spread, and accordingly, these portable electronic devices are becoming thinner, smaller, and lighter. Thus, thorough research into manufacturing secondary batteries serving as power sources thereof, which are small and lightweight, are capable of charging and discharging for a long time, and have increased high-rate characteristics, is ongoing.

20 [0003] Secondary batteries are classified into lead-acid batteries, nickelcadmium (Ni-Cd) batteries, nickel-hydrogen (Ni-MH) batteries, lithium batteries, and the like, depending on the type of anode material or cathode material, and the potential and energy density thereof are determined by unique characteristics of the electrode materials. Thereamong, lithium secondary batteries have high energy density due to low oxidation/reduction potential and molecular weight of lithium and are thus mainly used as power sources for driving portable electronic devices such as laptop computers, camcorders, and mobile phones. However, lithium secondary batteries have a major problem in that safety thereof is deteriorated during continuous charging. One of causes that may affect battery stability is heat generation due to structural collapse of the cathode, and the battery stability based on the principle of operation of a secondary battery, especially 25 a non-aqueous electrolyte secondary battery, is described below. Specifically, the cathode active material of the non-aqueous electrolyte secondary battery includes lithium-containing metal oxide capable of intercalating and deintercalating lithium and/or lithium ions. Such a cathode active material is modified into a thermally unstable structure because a large amount of lithium is deintercalated during overcharging. In this overcharged state, when the battery temperature reaches 30 a critical temperature due to external physical impact, such as exposure to high temperatures, etc., oxygen is released from the cathode active material having an unstable structure, and the released oxygen causes exothermic decomposition reaction with the solvent of the electrolyte solution. In particular, since combustion of the electrolyte solution is further accelerated by oxygen released from the cathode, ignition and rupture of the battery due to thermal runaway are caused by this chain of exothermic reactions. In addition, the cathode transition metal precipitated on the anode acts as a catalyst that accelerates decomposition of the non-aqueous electrolyte, generating gas inside the battery, or interfering with 35 movement of lithium ions due to the SEI layer of the anode during charging/discharging, ultimately greatly lowering battery performance and efficiency.

40 [0004] Meanwhile, in a battery with a high-capacity Ni-rich cathode, residual lithium (LiOH, Li₂CO₃) and residual water may promote side reactions of lithium salts in the non-aqueous electrolyte solution. Byproducts are generated through side reactions of lithium salts in the non-aqueous electrolyte solution, which causes discoloration of the electrolyte solution and impairs battery characteristics.

45 [0005] With the goal of solving the above problems, therefore, Japanese Patent Application Publication No. 2013-157305 discloses an electrolyte solution including a compound having two isocyanate groups, and Korean Patent No. 10-0412522 discloses an electrolyte solution including di-t-butylsilyl bis(trifluoromethanesulfonate), trimethylsilyl methanesulfonate, trimethylsilyl benzenesulfonate, trimethylsilyl trifluoromethanesulfonate, triethylsilyl trifluoromethanesulfonate, etc., but there is still a need for research into electrolyte solutions with excellent room-temperature and high-temperature thermal stability and high-temperature storability.

50 [0006] Currently, development of additives capable of improving thermal stability and high-temperature storability of secondary batteries is required.

55 [0007] Accordingly, the present inventors have made great efforts to solve such problems, and thus ascertained that, when a compound of Chemical Formula 1 or Chemical Formula 2 is added to a non-aqueous electrolyte solution, generation of byproducts in the electrolyte solution may be suppressed by virtue of stabilization of the non-aqueous electrolyte solution, such that discoloration due to decomposition of the electrolyte solution may be prevented, and battery internal resistance characteristics may be improved and high-temperature storage efficiency (capacity retention/recovery) may be increased, thus culminating in the present invention. In addition, the present invention has a structure different and distinguished from conventional additives that stabilize electrolyte solutions, and has superior performance.

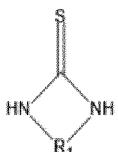
[Disclosure]

[0008] It is an object of the present invention to provide a non-aqueous electrolyte solution for a secondary battery with increased room-temperature and high-temperature thermal stability and high-temperature storability.

5 [0009] It is another object of the present invention to provide a secondary battery having excellent room-temperature and high-temperature thermal stability and high-temperature storability.

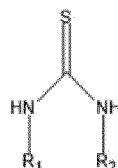
[0010] In order to accomplish the above objects, the present invention provides a non-aqueous electrolyte solution for a secondary battery including (A) a lithium salt, (B) a non-aqueous organic solvent, and (C) at least one additive selected from the group consisting of a compound represented by Chemical Formula 1 and a compound represented by Chemical Formula 2 below.

10 [Chemical Formula 1]



20 [0011] In Chemical Formula 1, R₁ is independently a C1-C3 alkyl.

25 [Chemical Formula 2]



35 [0012] In Chemical Formula 2, R₁ and R₂ are each independently a hydrogen atom or a C1-C9 alkyl.

[0013] In addition, the present invention provides a secondary battery including (a) a cathode including a cathode active material capable of intercalating and deintercalating lithium, (b) an anode including an anode active material capable of intercalating and deintercalating lithium, (c) the electrolyte solution described above, and (d) a separator.

35 [Mode for Invention]

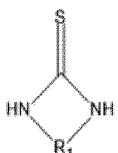
40 [0014] Unless otherwise defined, all technical and scientific terms used herein have the same meanings as typically understood by those skilled in the art to which the present invention belongs. In general, the nomenclature used herein is well known in the art and is typical.

[0015] In the present invention, a non-aqueous electrolyte solution for a secondary battery is stabilized by adding an additive, which is a compound of Chemical Formula 1 or Chemical Formula 2, to the non-aqueous electrolyte solution, thus suppressing generation of byproducts in the electrolyte solution, thereby preventing discoloration due to decomposition of the electrolyte solution, and improving battery internal resistance characteristics and increasing high-temperature storage efficiency (capacity retention/recovery).

[0016] Accordingly, an aspect of the present invention pertains to a non-aqueous electrolyte solution for a secondary battery including (A) a lithium salt, (B) a non-aqueous organic solvent, (C) at least one additive selected from the group consisting of a compound represented by Chemical Formula 1 and a compound represented by Chemical Formula 2 below.

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[Chemical Formula 1]

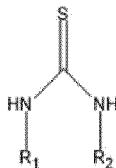


[0017] In Chemical Formula 1, R₁ is independently a C1-C3 alkyl.

[Chemical Formula 2]

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[0018] In Chemical Formula 2, R₁ and R₂ are each independently a hydrogen atom or a C1-C9 alkyl.

[0019] Another aspect of the present invention pertains to a secondary battery including (a) a cathode including a cathode active material capable of intercalating and deintercalating lithium, (b) an anode including an anode active material capable of intercalating and deintercalating lithium, (c) the electrolyte solution described above, and (d) a separator.

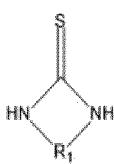
[0020] Hereinafter, a detailed description will be given of the present invention.

[0021] The non-aqueous electrolyte solution for a secondary battery according to the present invention includes (A) a lithium salt, (B) a non-aqueous organic solvent, and (C) at least one additive selected from the group consisting of a compound represented by Chemical Formula 1 and a compound represented by Chemical Formula 2 below.

[Chemical Formula 1]

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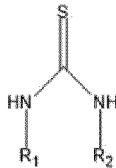


[0022] In Chemical Formula 1,
R₁ is independently a C1-C3 alkyl.

[Chemical Formula 2]

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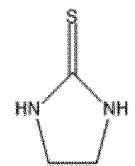
[0023] In Chemical Formula 2,

R₁ and R₂ are each independently a hydrogen atom or a C1-C9 alkyl.

[0024] In the present invention, the compound represented by Chemical Formula 1 is preferably 2-imidazolidine, which is a compound represented by Chemical Formula 1-1 below.

[Chemical Formula 1-1]

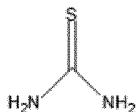
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[0025] In the present invention, the compound represented by Chemical Formula 2 is preferably thiourea, which is a compound represented by Chemical Formula 2-1 below.

[Chemical Formula 2-1]

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[0026] In the present invention, at least one lifespan prolonging additive or anode film forming additive selected from the group consisting of vinyl carbonate, vinyl ethylene carbonate, fluoroethylene carbonate, and tetrahydrofuro[3,2-b]furan-2,5-dione (also referred to as muconic lactone) may be further included.

[0027] In the present invention, at least one high-temperature performance enhancing additive selected from the group consisting of 1,3-propane sultone, 1,3-propene-1,3-sultone, ethylene sulfate, 1,4-butane sultone, 1,3-propanediol cyclic sulfate, 4,4'-bi-1,3,2-dioxathiolane-2,2,2',2'-tetraoxide, 1,3-divinyltetramethyldisiloxane, and 2,4,8,10-tetraoxa-3,9-dithiaspiro[5.5]undecane (or referred to as 3,3,9,9-tetraoxide) may be further included.

[0028] In the present invention, at least one power enhancing additive selected from the group consisting of aromatic phosphate compounds, such as bis(trimethylsilyl) sulfate, bis(trimethylsilyl) sulfate, trimethylsilyl ethenesulfonate, triethylsilyl ethenesulfonate, and tetraphenyl (propane-2,2-diylbis(4,1-phenylene)) bis(phosphate) may be further included.

[0029] In the present invention, at least one high-temperature performance and power enhancing additive selected from the group consisting of lithium difluorophosphate, lithium bis(oxalato)borate, lithium bis(fluorosulfonyl)imide, lithium bis(trifluoromethanesulfonyl)imide, cesium hexafluorophosphate, cesium bis(fluorosulfonyl)imide, cesium bis(trifluoromethanesulfonyl)imide, lithium difluoro(oxalato)borate, lithium tetrafluoro oxalato phosphate, lithium difluoro bis(oxalato) phosphate, and lithium bis(phosphorodifluoride) triethylammonium ethenesulfonate may be further included.

[0030] In the present invention, the lithium salt used as the solute of the electrolyte may be at least one selected from the group consisting of LiPF₆, LiBF₄, LiSbF₆, LiAsF₆, LiClO₄, LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)₂, CF₃SO₃Li, and LiC(CF₃SO₂)₃. The concentration of the lithium salt is preferably set in the range of 0.1 M to 2.0 M, more preferably 0.7 M to 1.6 M. If the concentration thereof is less than 0.1 M, the conductivity of the electrolyte solution may decrease and the performance of the electrolyte solution may deteriorate, whereas if it exceeds 2.0 M, mobility of lithium ions may decrease due to an increase in the viscosity of the electrolyte solution. These lithium salts act as a source of lithium ions in the battery, enabling basic operation of the lithium secondary battery.

[0031] In the present invention, the non-aqueous organic solvent may be at least one selected from the group consisting of linear carbonate, cyclic carbonate, linear ester, and cyclic ester. Here, the linear carbonate may be at least one carbonate selected from the group consisting of dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, ethyl methyl carbonate, and mixtures thereof, the cyclic carbonate may be at least one carbonate selected from the group consisting of ethylene carbonate (EC), propylene carbonate (PC), 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-pentylene carbonate, 2,3-pentylene carbonate, vinylene carbonate (VC), vinyl ethylene carbonate, and fluoroethylene carbonate, the linear ester may be at least one ester selected from the group consisting of methyl propionate, ethyl propionate, propyl acetate, butyl acetate, and ethyl acetate, and the cyclic ester may be at least one ester selected from the group consisting of gamma-butyrolactone, caprolactone, and valerolactone.

[0032] In the present invention, the amount of at least one additive selected from the group consisting of a compound represented by Chemical Formula 1 and a compound represented by Chemical Formula 2 may be 10 to 100,000 ppm, preferably 20 to 80,000 ppm, more preferably 50 to 50,000 ppm, based on the total amount of the electrolyte solution for a secondary battery. If the amount thereof is less than 10 ppm, high-temperature battery characteristics may be deteriorated, whereas if it exceeds 100,000 ppm, ionic conductivity may be lowered.

[0033] The electrolyte solution for a lithium ion secondary battery according to the present invention usually maintains stability in a temperature range of -20 to 50°C. The electrolyte solution of the present invention may be applied to lithium ion secondary batteries, lithium ion polymer batteries, and the like.

[0034] In the lithium secondary battery of the present invention, the cathode material may include lithium metal oxide such as LiCoO₂, LiNiO₂, LiMnO₂, LiMn₂O₄, or LiNi_{1-x-y}Co_xM_yO₂ (0≤x≤1, 0≤y≤1, 0≤x+y≤1, M is a metal such as Al, Sr, Mg, La, etc.), and the anode material may include crystalline or amorphous carbon, carbon composites, lithium metal, or lithium alloys. A lithium ion secondary battery is manufactured in a manner in which each active material is applied at an appropriate thickness and length onto a thin current collector, or is applied alone in a film form and wound or stacked along with a separator, which is an insulator, to form an electrode group, which is then placed in a can or similar container, followed by injection of a non-aqueous electrolyte solution containing trialkylsilyl sulfate and phosphite-based stabilizers. Here, the separator used may be resin such as polyethylene, polypropylene, etc.

[0035] A better understanding of the present invention may be obtained through the following examples. These examples are merely set forth to illustrate the present invention, and are not to be construed as limiting the scope of the present invention, as will be obvious to those skilled in the art.

5 [Examples]

Example 1

[0036] A cathode slurry was prepared in a manner in which $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ as a cathode active material, polyvinylidene fluoride (PVdF) as a binder, and carbon black as a conductive material were mixed in a weight ratio of 95.6:2.2:2.2 and then dispersed in N-methyl-2-pyrrolidone. This slurry was applied onto an aluminum foil having a thickness of 20 μm , dried, and rolled, thereby manufacturing a cathode.

[0037] An anode active material slurry was prepared in a manner in which natural graphite as an anode active material, acetylene black as a conductive material, and polyvinylidene fluoride (PVdF) as a binder were mixed in a weight ratio of 85:8:7 and then dispersed in N-methyl-2-pyrrolidone. This slurry was applied onto a copper foil having a thickness of 15 μm , dried, and rolled, thereby manufacturing an anode.

[0038] A film separator made of polyethylene (PE) with a thickness of 20 μm was stacked between the electrodes manufactured above, wound, and pressed to form a cell using a pouch having a size of 6 mm in thickness x 35 mm in width x 60 mm in length, and the following non-aqueous electrolyte solution was injected thereto, ultimately manufacturing a lithium secondary battery (NCM811/AG (890 mAh)).

[0039] The electrolyte solution was prepared by dissolving LiPF_6 at 1.0 M in a mixed solvent of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) (1:1 (v/v)) and then adding 0.02 wt% of 2-imidazolidinethione thereto.

Examples 2 to 28

[0040] These examples were performed in the same manner as in Example 1, with the exception that electrolyte solutions and 2-imidazolidinethione or thiourea were added in the amounts shown in Tables 1 to 5 below.

[Table 1]

Additive (wt%)			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
2-imidazolidinethione 1.0 M LiPF_6 in EC/EMC=1/1 (v/v)			0.02	0.1	0.3			
2-imidazolidinethione 1.0 M LiPF_6 in EC/DMC=1/1 (v/v)						0.02	0.1	0.3
Room-temperature (25°C) thermal stability evaluation	APHA (-)	Beginning	3	2	2	3	3	2
		After 1 month	6	6	4	6	6	4
High-temperature (60°C) thermal stability evaluation	APHA (-)	Beginning	3	2	2	3	3	2
		After 1 month	8	8	5	9	8	5

[Table 2]

Additive (wt%)		Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
2-imidazolidinethione 1.0 M	LiPF ₆ in EC/DEC=1/1 (v/v)	0.02	0.1	0.3			
2-imidazolidinethione 1.0 M	LiPF ₆ in EC/PC=1/1 (v/v)				0.02	0.1	0.3
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	3	3	7	7	4
		After 1 month	5	5	9	9	7
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	3	3	7	7	4
		After 1 month	7	7	5	9	5

[Table 3]

Additive (wt%)			Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
2-imidazolidinethione 1.0 M LiPF ₆ in EC/EP=1/1 (v/v)			0.02	0.1	0.3			
2-imidazolidinethione 1.0 M LiPF ₆ in EC/EA=1/1 (v/v)						0.02	0.1	0.3
Room-temperature (25°C) thermal stability evaluation	APHA (-)	Beginning	3	3	2	3	3	2
		After 1 month	5	5	4	6	6	5
High-temperature (60°C) thermal stability evaluation	APHA (-)	Beginning	3	3	2	3	3	2
		After 1 month	8	7	6	9	7	5

[Table 4]

Additive (wt%)			Example 19	Example 20	Example 21
2-imidazolidinethione 0.5 M LiPF ₆ , 0.5 M LiFSI in EC/EMC=1/1 (v/v)			0.02	0.1	0.3
Room-temperature (25°C) thermal stability evaluation	APHA (-)	Beginning	4	4	2
		After 1 month	7	7	6
High-temperature (60°C) thermal stability evaluation	APHA (-)	Beginning	4	4	2
		After 1 month	11	9	6

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[Table 5]

Additive (wt%)	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27	Example 28
Thiourea 1.0 M LiPF ₆ in EC/EP=1/1 (v/v)	0.1						
Thiourea 1.0 M LiPF ₆ in EC/DMC=1/1 (v/v)		0.1					
Thiourea 1.0 M LiPF ₆ in EC/DEC=1/1 (v/v)			0.1				
Thiourea			0.1				
1.0 M LiPF ₆ in EC/PC=1/1 (v/v)							
Thiourea 1.0 M LiPF ₆ in EC/EP=1/1 (v/v)						0.1	
Thiourea 1.0 M LiPF ₆ in EC/EA=1/1 (v/v)							0.1
Thiourea 0.5 M LiPF ₆ , 0.5 M LiFSI in EC/EMC=1/1 (v/v)							
Room-temperature (25°C) thermal stability evaluation	Beginning	3	4	4	8	4	4
	APHA(-)	After 1 month	7	7	6	10	6
High-temperature (60°C) thermal stability evaluation	Beginning	3	4	4	8	4	4
	APHA(-)	After 1 month	9	9	10	8	8

Comparative Examples 1 to 7

[0041] Respective lithium secondary batteries were manufactured in the same manner as above, with the exception that 2-imidazolidinethione was not added to electrolyte solutions as shown in Table 6 below.

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[Table 6]

Additive (wt%)	Com. Example 1	Com. Example 2	Com. Example 3	Com. Example 4	Com. Example 5	Com. Example 6	Com. Example 7
2 -imidazo lidinethio ne/thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)	0						
2 -imidazo lidinethio ne/thiourea 1.0 M LiPF ₆ in EC/DMC=1/1 (v/v)	0						
2 -imidazo lidinethio ne/thiourea 1.0 M LiPF ₆ in EC/DEC=1/1 (v/v)	0						
2 -imidazo lidinethio ne/thiourea 1.0 M LiPF ₆ in EC/PC=1/1 (v/v)		0					
2 -imidazo lidinethio ne/thiourea 1.0 M LiPF ₆ in EC/EP=1/1 (v/v)			0				
2 -imidazo lidinethio ne/thiourea 1.0 M LiPF ₆ in EC/EA=1/1 (v/v)				0			
2 -imidazo lidinethio ne/thiourea 0.5 M LiPF ₆ , 0.5 M LiFSI in EC/EMC=1/1 (v/v)					0		
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	10	12	10	15	11
		After 1 month	35	41	31	42	36
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	10	12	10	15	11
		After 1 month	82	90	79	101	78
						80	107

Examples 29 to 73

[0042] These examples were performed in the same manner as in Example 2, with the exception that a lifespan prolonging additive, a high-temperature performance enhancing additive, a power enhancing additive, or a high-temperature performance and power enhancing additive was further added in the amounts shown in Tables 7 to 14 below.

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[Table 7]

Additive (w%)	Example 2	Example 29	Example 30	Example 31	Example 32	Example 33
2-imidazolidinethione 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)	0.1	0.1	0.1	0.1	0.1	0.1
Chemical Formula A-1	1					
Chemical Formula A-2		1				
Chemical Formula A-3			1			
Chemical Formula A-4				1		
Chemical Formula B-1					2	
Chemical Formula B-2						
Chemical Formula B-3						
Chemical Formula B-4						
Chemical Formula B-5						
Chemical Formula B-6						
Chemical Formula B-7						
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	6	6	8	9
		After 1 month	2	3	4	5
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	6	6	8	9
		After 1 month	3	3	6	7
High-temperature storage evaluation (70°C, 1 week)	AC-IR	Change (%)	80.5%	68.6%	69.7%	73.9%
	Retention capacity	Capacity retention (%)	70.6%	78.8%	81.4%	75.5%
	Recovery capacity	Capacity recovery (%)	75.7%	83.6%	85.5%	81.2%
					80.6%	88.8%

[Table 8]

Additive (wt%)	Example 34	Example 35	Example 36	Example 37	Example 38	Example 39
2-imidazolidinethione 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)	0.1	0.1	0.1	0.1	0.1	0.1
Chemical Formula A-1						
Chemical Formula A-2						
Chemical Formula A-3						
Chemical Formula A-4						
Chemical Formula B-1						
Chemical Formula B-2	2					
Chemical Formula B-3	2					
Chemical Formula B-4		2				
Chemical Formula B-5			2			
Chemical Formula B-6				2		
Chemical Formula B-7					2	
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	7 3	9 5	6 2	6 2
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	7 6	9 7	6 6	6 6
High-temperature storage evaluation (70°C, 1 week)	AC-IR Retention capacity Recovery capacity	Change (%) Capacity retention (%) Capacity recovery (%)	80.2% 73.4% 76.8%	76.1% 82.6% 87.4%	78.7% 74.4% 79.6%	74.4% 80.5% 86.6%

[Table 9]

Additive (wt%)	Example 40	Example 41	Example 42	Example 43	Example 44	Example 45
2-imidazolidinethione 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)	0.1	0.1	0.1	0.1	0.1	0.1
Chemical Formula C-1	1					
Chemical Formula C-2		1				
Chemical Formula C-3			1			
Chemical Formula C-4				1		
Chemical Formula C-5					1	
Chemical Formula D-1						1
Chemical Formula D-2						
Chemical Formula D-3						
Chemical Formula D-4						
Chemical Formula D-5						
Chemical Formula D-6						
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	7 3	9 5	9 6	6 2
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	7 6	9 7	9 7	6 6
High-temperature storage evaluation (70°C, 1 week)	AC-IR Retention capacity Recovery capacity	Change (%) Capacity retention (%) Capacity recovery (%)	61.5% 77.7% 85.9%	68.7% 74.7% 83.1%	57.8% 81.4% 86.6%	60.5% 78.4% 86.2%
					69.3%	35.6%
					74.2%	85.6%
					88.6%	94.5%

[Table 10]

	Additive (wt%)	Example 46	Example 47	Example 48	Example 49	Example 50	
5	2-imidazolidinethione 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)	0.1	0.1	0.1	0.1	0.1	
10	Chemical Formula C-1						
15	Chemical Formula C-2						
20	Chemical Formula C-3						
25	Chemical Formula C-4						
30	Chemical Formula D-1						
35	Chemical Formula D-2	1					
40	Chemical Formula D-3		1				
45	Chemical Formula D-4			1			
50	Chemical Formula D-5				1		
55	Chemical Formula D-6					1	
25	Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	6	6	6	6
			After 1 month	2	2	2	2
30	High-temperature(60°C) thermal stability evaluation	APHA(-)	Beginning	6	6	6	6
			After 1 month	3	4	4	3
35	High-temperature storage evaluation (70°C, 1 week)	AC-IR	Change (%)	48.7%	43.5%	41.4%	40.9%
		Retention capacity	Capacity retention (%)	77.7%	79.2%	83.6%	84.7%
		Recovery capacity	Capacity recovery (%)	85.6%	87.6%	91.1%	92.1%
40							85.5%
45							93.4%

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[Table 11]

Additive (wt%)	Example 51	Example 52	Example 53	Example 54	Example 55	Example 56
Thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)	0.1	0.1	0.1	0.1	0.1	0.1
Chemical Formula A-1	1					
Chemical Formula A-2		1				
Chemical Formula A-3			1			
Chemical Formula A-4				1		
Chemical Formula B-1					2	
Chemical Formula B-2						
Chemical Formula B-3						
Chemical Formula B-4						
Chemical Formula B-5						
Chemical Formula B-6						
Chemical Formula B-7						
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	7 3	7 4	9 5	10 6
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	7 4	7 4	9 7	10 7
High-temperature storage evaluation (70°C, 1 week)	AC-IR Retention capacity Recovery capacity	Change (%) Capacity retention (%) Capacity recovery (%)	82.5% 69.1% 74.2%	70.6% 77.3% 82.1%	71.7% 79.9% 84.0%	75.9% 74.0% 79.7%
					76.6% 73.1% 79.1%	77.2% 81.2% 87.3%

Table 12]

Additive (wt%)	Example 57	Example 58	Example 59	Example 60	Example 61	Example 62	
Tthiourea	0.1	0.1	0.1	0.1	0.1	0.1	
1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)							
Chemical Formula A-1							
Chemical Formula A-2							
Chemical Formula A-3							
Chemical Formula A-4							
Chemical Formula B-1							
Chemical Formula B-2		2					
Chemical Formula B-3			2				
Chemical Formula B-4				2			
Chemical Formula B-5					2		
Chemical Formula B-6						2	
Chemical Formula B-7							2
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	8	10	7	7	7
		After 1 month	4	6	3	3	4
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	8	10	7	7	7
		After 1 month	7	8	7	7	7
High-temperature storage evaluation (70°C, 1 week)	AC-IR	Change (%)	82.2%	78.1%	80.7%	76.4%	77.5%
	Retention capacity	Capacity retention (%)	71.9%	81.1%	72.9%	79.0%	78.3%
	Recovery capacity	Capacity recovery (%)	75.3%	85.9%	78.1%	85.1%	81.8%
							87.7%

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[Table 13]

Additive (wt%)	Example 63	Example 64	Example 65	Example 66	Example 67	Example 68
Thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)	0.1	0.1	0.1	0.1	0.1	0.1
Chemical Formula C-1	1					
Chemical Formula C-2		1				
Chemical Formula C-3			1			
Chemical Formula C-4				1		
Chemical Formula C-5					1	
Chemical Formula D-1						1
Chemical Formula D-2						
Chemical Formula D-3						
Chemical Formula D-4						
Chemical Formula D-5						
Chemical Formula D-6						
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	8 4	10 6	10 7	7 3
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning After 1 month	8 7	10 8	10 8	7 5
High-temperature storage evaluation (70°C, 1 week)	AC-IR Retention capacity Recovery capacity	Change (%) Capacity retention (%) Capacity recovery (%)	63.5% 76.2% 84.4%	70.7% 73.2% 81.6%	59.8% 79.9% 85.1%	62.5% 76.9% 84.7%
						71.3% 72.2% 86.6%
						37.6% 84.1% 93.0%

[Table 14]

Additive (wt%)			Example 69	Example 70	Example 71	Example 72	Example 73
Thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)			0.1	0.1	0.1	0.1	0.1
Chemical Formula C-1							
Chemical Formula C-2							
Chemical Formula C-3							
Chemical Formula C-4							
Chemical Formula D-1							
Chemical Formula D-2		1					
Chemical Formula D-3				1			
Chemical Formula D-4					1		
Chemical Formula D-5						1	
Chemical Formula D-6							1
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	7	7	7	7	7
		After 1 month	3	3	3	3	3
High-temperature(60°C) thermal stability evaluation	APHA(-)	Beginning	7	7	7	7	7
		After 1 month	4	5	5	4	4
High-temperature storage evaluation (70°C, 1 week)	AC-IR	Change (%)	50.7%	45.5%	43.4%	42.9%	40.2%
	Retention capacity	Capacity retention (%)	76.2%	77.7%	82.1%	83.2%	84.0%
	Recovery capacity	Capacity recovery (%)	84.1%	86.1%	89.6%	90.6%	91.9%

Comparative Examples 8 to 29

[0043] These comparative examples were performed in the same manner as in Comparative Example 1, with the exception that a lifespan prolonging additive, a high-temperature performance enhancing additive, a power enhancing additive, or a high-temperature performance and power enhancing additive was further added in the amounts shown in Tables 15 to 18 below.

[Table 15]

Additive (wt%)	Com. Example 1	Com. Example 8	Com. Example 9	Com. Example 10	Com. Example 11	Com. Example 12
2-imidazolidinethione/thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)						
Chemical Formula A-1	1					
Chemical Formula A-2		1				
Chemical Formula A-3			1			
Chemical Formula A-4				1		
Chemical Formula B-1					1	
Chemical Formula B-2						2
Chemical Formula B-3						
Chemical Formula B-4						
Chemical Formula B-5						
Chemical Formula B-6						
Chemical Formula B-7						
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	10	10	13	15
		After 1 month	35	38	43	50
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	10	10	13	15
		After 1 month	82	88	90	101
AC-IR	Change (%)	85.2%	70.1%	71.2%	76.5%	77.5%
High-temperature storage evaluation (70°C, 1 week)	Retention capacity	64.2%	75.9%	78.3%	72.2%	72.4%
	Recovery capacity	68.7%	80.6%	82.2%	78.8%	77.6%

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[Table 16]

Additive (wt%)	Com. Example 13	Com. Example 14	Com. Example 15	Com. Example 16	Com. Example 17	Com. Example 18
2-imidazolidinethione/thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)						
Chemical Formula A-1						
Chemical Formula A-2						
Chemical Formula A-3						
Chemical Formula A-4						
Chemical Formula B-1						
Chemical Formula B-2	2					
Chemical Formula B-3		2				
Chemical Formula B-4			2			
Chemical Formula B-5				2		
Chemical Formula B-6					2	
Chemical Formula B-7						2
Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	12	15	10	11
		After 1 month	44	50	46	39
High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	12	15	10	11
		After 1 month	110	130	105	105
High-temperature storage evaluation (70°C, 1 week)	AC-IR	Change (%)	85.2%	80.9%	83.1%	78.9%
	Retention capacity	Capacity retention (%)	70.8%	79.7%	71.1%	78.6%
	Recovery capacity	Capacity recovery (%)	72.1%	84.3%	74.3%	83.9%
					80.2%	86.4%

[Table 17]

5	Additive (wt%)	Com. Example 19	Com. Example 20	Com. Example 21	Com. Example 22	Com. Example 23	Com. Example 24		
10	2 -imidazo lidinethio ne/ thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)								
15	Chemical Formula C-1	1							
20	Chemical Formula C-2		1						
25	Chemical Formula C-3			1					
30	Chemical Formula C-4				1				
35	Chemical Formula C-5					1			
40	Chemical Formula D-1						1		
45	Chemical Formula D-2								
50	Chemical Formula D-3								
55	Chemical Formula D-4								
	Chemical Formula D-5								
	Chemical Formula D-6								
40	Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	12	10	15	15	13	10
			After 1 month	50	52	56	60	40	36
45	High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	12	10	15	15	13	10
			After 1 month	130	150	140	160	97	78
50	High-temperature storage evaluation (70°C, 1 week)	AC-IR	Change (%)	66.0%	70.3%	60.1%	63.2%	70.4%	40.8%
		Retention capacity	Capacity retention (%)	74.1%	72.4%	78.8%	74.6%	72.1%	83.1%
		Recovery capacity	Capacity recovery (%)	82.6%	81.6%	83.4%	82.8%	81.7%	90.2%

[Table 18]

5	Additive (wt%)		Com. Example 25	Com. Example 26	Com. Example 27	Com. Example 28	Com. Example 29
10	2 -imidazo lidinethio ne/thiourea 1.0 M LiPF ₆ in EC/EMC=1/1 (v/v)						
15	Chemical Formula C-1						
20	Chemical Formula C-2						
25	Chemical Formula C-3						
30	Chemical Formula C-4						
35	Chemical Formula C-5						
40	Chemical Formula C-6						
45	Room-temperature (25°C) thermal stability evaluation	APHA(-)	Beginning	10	10	10	10
50			After 1 month	40	39	38	38
55	High-temperature (60°C) thermal stability evaluation	APHA(-)	Beginning	10	10	10	10
60			After 1 month	88	90	80	82
65	High-temperature storage evaluation (70°C, 1 week)	AC-IR	Change (%)	50.9%	48.6%	46.7%	45.6%
70		Retention capacity	Capacity retention (%)	73.9%	75.2%	80.1%	81.1%
75		Recovery capacity	Capacity recovery (%)	82.4%	84.6%	89.6%	91.8%

[0044]

45 Note) Chemical Formula A-1: vinyl carbonate
 Chemical Formula A-2: vinyl ethylene carbonate
 Chemical Formula A-3: fluoroethylene carbonate
 Chemical Formula A-4: muconic lactone or tetrahydrofuro[3,2-b]furan-2,5-dione
 Chemical Formula B-1: 1,3-propane sultone
 Chemical Formula B-2: 1,3-propene-1,3-sultone
 Chemical Formula B-3: ethylene sulfate
 Chemical Formula B-4: 1,4-butane sultone
 Chemical Formula B-5: 1,3-propanediol cyclic sulfate
 Chemical Formula B-6: 4,4'-bi-1,3,2-dioxathiolane-2,2,2',2'-tetraoxide
 Chemical Formula B-7: 2,4,8,10-tetraoxa-3,9-dithiaspiro[5.5]undecane or 3,3,9,9-tetraoxide
 Chemical Formula C-1: bis(trimethylsilyl) sulfate
 Chemical Formula C-2: bis(trimethylsilyl) sulfate

Chemical Formula C-3: trimethylsilyl ethenesulfonate
 Chemical Formula C-4: triethylsilyl ethenesulfonate
 Chemical Formula C-5: tetraphenyl (propane-2,2-diylbis(4,1-phenylene)) bis(phosphate)
 Chemical Formula D-1: lithium difluorophosphate
 5 Chemical Formula D-2: lithium bis(oxalato)borate
 Chemical Formula D-3: lithium bis(fluorosulfonyl)imide
 Chemical Formula D-4: lithium difluoro(oxalato)borate
 Chemical Formula D-5: lithium tetrafluoro oxalato phosphate
 Chemical Formula D-6: lithium difluoro bis(oxalato) phosphate
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Property Evaluation 1: Evaluation of room-temperature thermal stability

[0045] Thermal stability of the manufactured battery was measured at 25°C for 1 month at weekly intervals using a colorimeter (GNB Tech). APHA levels were represented at the beginning and after 1 month.

Property Evaluation 2: Evaluation of high-temperature thermal stability

[0046] Thermal stability was measured at 60°C for 1 week at daily intervals using a colorimeter (GNB Tech). APHA levels were represented at the beginning and after 1 week.

Property Evaluation 3: Evaluation of high-temperature storage

[0047]

1) Internal resistance (AC-IR): After charging the manufactured battery to 4.2 V at 1C, internal resistance (AC-IR) was measured using a resistance meter (HIOKI, Japan), and the battery was charged to 4.2 V at 1C and then stored at a high temperature (70°C) for 7 days, followed by charging to 4.2 V at 1C and discharging at 1C twice, and internal resistance (AC-IR) was then measured using a resistance meter (HIOKI, Japan) after storage at a high temperature (70°C).

2) Retention, Recovery capacity: The battery was charged to 4.2 V at 1C, stored at a high temperature (70°C) for 7 days, and then discharged to 2.75 V at 1C, and retention capacity (discharge capacity) was measured, and also, the battery was charged again to 4.2 V at 1C and then discharged to 2.75 V at 1C, after which recovery capacity (discharge capacity) was measured and represented as a percentage relative to the initial discharge capacity.

[0048] As shown in Tables 1 to 18, the electrolyte solutions of Examples 1 to 73 of the present invention exhibited enhanced lifespan and high-temperature storage evaluation results compared to Comparative Examples 1 to 29 in room-temperature and high-temperature thermal stability evaluation and high-temperature storage evaluation.

[0049] As is apparent from Examples of the present invention, the additive of the present invention is effective at stabilizing the non-aqueous electrolyte solution, thus suppressing generation of byproducts in the electrolyte solution by virtue of stabilization of the non-aqueous electrolyte solution, thereby (1) preventing discoloration due to decomposition of the electrolyte solution and (2) improving battery internal resistance characteristics and increasing high-temperature storage efficiency (capacity retention/recovery).

[0050] As shown in Tables 1 to 4, the non-aqueous electrolyte solutions in which 2-imidazolidinethione was added according to Examples 1 to 21 of the present invention exhibited very low or almost no color change at room temperature and high temperature compared to Comparative Examples 1 to 7 of Table 6 in which 2-imidazolidinethione was not added. Moreover, the color change was confirmed to significantly decrease with an increase in the amount of 2-imidazolidinethione.

[0051] In addition, as shown in Table 5, the non-aqueous electrolyte solutions in which thiourea was added according to Examples 22 to 28 of the present invention exhibited very low or almost no color change at room temperature and high temperature compared to Comparative Examples 1 to 7 of Table 6 in which thiourea was not added.

[0052] As shown in Table 7, the electrolyte solution of Example 2 of the present invention in which 0.1 wt% of 2-imidazolidinethione was added exhibited a very low color change at room temperature and high temperature compared to Comparative Example 1 of Table 15, and manifested superior performance in battery internal resistance and high-temperature storage efficiency evaluation. As in Examples 29 to 50, when the lifespan prolonging additive, the high-temperature performance enhancing additive, the power enhancing additive, or the high-temperature performance and power enhancing additive was further added, battery performance was further enhanced. Moreover, the electrolyte solutions of Examples 29 to 50 exhibited a very low color change at room temperature and high temperature compared to Comparative Examples 8 to 29 in which 2-imidazolidinethione was not added, and also, battery internal resistance

was improved by about 5 to 45%, and capacity retention and recovery after storage at a high temperature were increased by about 3 to 15%.

[0053] Similarly, as shown in Table 11, the electrolyte solution of Example 51 of the present invention in which 0.1 wt% of thiourea was added exhibited a very low color change at room temperature and high temperature compared to Comparative Example 1 of Table 15, and also showed superior performance in battery internal resistance and high-temperature storage efficiency evaluation. As in Examples 52 to 73, when the lifespan prolonging additive, the high-temperature performance enhancing additive, the power enhancing additive, or the high-temperature performance and power enhancing additive was further added, battery performance was further enhanced. Also, the electrolyte solutions of Examples 52 to 73 exhibited a very low color change at room temperature and high temperature compared to Comparative Examples 8 to 29 in which thiourea was not added, and battery internal resistance was improved by about 2 to 45%, and capacity retention and recovery after storage at a high temperature were increased by about 3 to 15%.

[industrial Applicability]

[0054] According to the present invention, a non-aqueous electrolyte solution is stabilized by adding a compound of Chemical Formula 1 or Chemical Formula 2 thereto, thus suppressing generation of byproducts in the electrolyte solution, thereby preventing discoloration due to decomposition of the electrolyte solution, and improving battery internal resistance characteristics and increasing high-temperature storage efficiency (capacity retention/recovery).

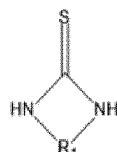
[0055] Having described specific parts of the present invention in detail above, it will be obvious to those skilled in the art that these specific descriptions are only preferred embodiments, and the scope of the present invention is not limited thereby. Accordingly, the substantial scope of the present invention will be defined by the appended claims and equivalents thereto.

Claims

1. A non-aqueous electrolyte solution for a secondary battery, comprising:

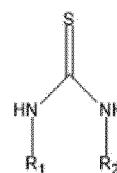
- (A) a lithium salt;
- (B) a non-aqueous organic solvent; and
- (C) at least one additive selected from the group consisting of a compound represented by Chemical Formula 1 and a compound represented by Chemical Formula 2:

[Chemical Formula 1]



in Chemical Formula 1, R₁ is independently a C1-C3 alkyl; and

[Chemical Formula 2]



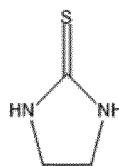
in Chemical Formula 2, R₁ and R₂ are each independently a hydrogen atom or a C1-C9 alkyl.

2. The non-aqueous electrolyte solution for a secondary battery of claim 1, wherein the compound represented by Chemical Formula 1 is a compound represented by Chemical Formula 1-1:

[Chemical Formula 1-1]

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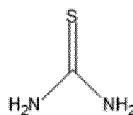


3. The non-aqueous electrolyte solution for a secondary battery of claim 1, wherein the compound represented by Chemical Formula 2 is a compound represented by Chemical Formula 2-1:

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[Chemical Formula 2-1]

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4. The non-aqueous electrolyte solution for a secondary battery of claim 1, wherein the lithium salt is at least one selected from the group consisting of LiPF₆, LiBF₄, LiSbF₆, LiAsF₆, LiClO₄, LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)₂, CF₃SO₃Li, and LiC(CF₃SO₂)₃.

5. The non-aqueous electrolyte solution for a secondary battery of claim 4, wherein the lithium salt is contained at a concentration of 0.1 to 2.0 M in the non-aqueous organic solvent.

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6. The non-aqueous electrolyte solution for a secondary battery of claim 1, wherein the non-aqueous organic solvent is at least one selected from the group consisting of linear carbonate, cyclic carbonate, linear ester, and cyclic ester.

7. The non-aqueous electrolyte solution for a secondary battery of claim 6, wherein:

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the linear carbonate is at least one carbonate selected from the group consisting of dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, ethyl methyl carbonate, and mixtures thereof,

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the cyclic carbonate is at least one carbonate selected from the group consisting of ethylene carbonate, propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-pentylene carbonate, 2,3-pentylene carbonate, vinylene carbonate, vinyl ethylene carbonate, and fluoroethylene carbonate,

the linear ester is at least one ester selected from the group consisting of methyl propionate, ethyl propionate, propyl acetate, butyl acetate, and ethyl acetate, and

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the cyclic ester is at least one ester selected from the group consisting of gamma-butyrolactone, caprolactone, and valerolactone.

8. The non-aqueous electrolyte solution for a secondary battery of claim 6, wherein the non-aqueous organic solvent comprises the linear carbonate and the cyclic carbonate that are mixed in a volume ratio of 1:9 to 9:1.

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9. The non-aqueous electrolyte solution for a secondary battery of claim 1, wherein an amount of the compound represented by Chemical Formula 1 or Chemical Formula 2 is 10 to 100,000 ppm based on a total amount of the electrolyte solution.

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10. The non-aqueous electrolyte solution for a secondary battery of claim 1, further comprising at least one lifespan prolonging additive selected from the group consisting of vinyl carbonate, vinyl ethylene carbonate, fluoroethylene carbonate, and tetrahydrofuro[3,2-b]furan-2,5-dione.

11. The non-aqueous electrolyte solution for a secondary battery of claim 1, further comprising at least one high-

temperature performance enhancing additive selected from the group consisting of 1,3-propane sultone, 1,3-propene-1,3-sultone, ethylene sulfate, 1,4-butane sultone, 1,3-propanediol cyclic sulfate, 4,4'-bi-1,3,2-dioxathiolane-2,2,2',2'-tetraoxide, 1,3-divinyltetramethylsiloxane, and 2,4,8,10-tetraoxa-3,9-dithiaspiro[5.5]undecane.

5 **12.** The non-aqueous electrolyte solution for a secondary battery of claim 1, further comprising at least one power enhancing additive selected from the group consisting of bis(trimethylsilyl) sulfate, bis(trimethylsilyl) sulfonate, trimethylsilyl ethenesulfonate, triethylsilyl ethenesulfonate, and tetraphenyl (propane-2,2-diylbis(4,1-phenylene)) bis(phosphate).

10 **13.** The non-aqueous electrolyte solution for a secondary battery of claim 1, further comprising at least one high-temperature performance and power enhancing additive selected from the group consisting of lithium difluorophosphate, lithium bis(oxalato)borate, lithium bis(fluorosulfonyl)imide, lithium bis(trifluoromethanesulfonyl)imide, cesium hexafluorophosphate, cesium bis(fluorosulfonyl)imide, cesium bis(trifluoromethanesulfonyl)imide, lithium difluoro(oxalato)borate, lithium tetrafluoro oxalato phosphate, lithium difluoro bis(oxalato) phosphate, and lithium bis(phosphorodifluoride) triethylammonium ethenesulfonate.

15 **14.** A lithium secondary battery, comprising:

20 (a) a cathode comprising a cathode active material capable of intercalating and deintercalating lithium;
 (b) an anode including an anode active material capable of intercalating and deintercalating lithium;
 (c) the non-aqueous electrolyte solution for a secondary battery of any one of claims 1 to 13; and
 (d) a separator.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/001751

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A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/0567(2010.01)i; H01M 10/052(2010.01)

According to International Patent Classification (IPC) or to both national classification and IPC

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M 10/0567(2010.01); H01M 10/052(2010.01); H01M 10/0562(2010.01); H01M 10/0565(2010.01);
H01M 10/36(2006.01); H01M 10/38(2006.01); H01M 4/96(2006.01)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models: IPC as above

Japanese utility models and applications for utility models: IPC as above

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal), STN (Registry, Caplus) & keywords: 비수성 전해액(non-aqueous electrolyte), 첨가제(additive),
이미다졸리딘티온(imidazolidinethione), 티오우레이(thiourea)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

25

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-0263849 B1 (SAMSUNG SDI CO., LTD.) 16 August 2000 (2000-08-16) See claim 1; paragraph [0001]; and the examples.	1,3-9,14
Y		10-13
A		2
Y	KR 10-2019-0078770 A (PANAX ETEC CO., LTD.) 05 July 2019 (2019-07-05) See claims 1, 3 and 10.	10-13
Y	KR 10-2019-0092880 A (PANAX ETEC CO., LTD.) 08 August 2019 (2019-08-08) See claims 1-5 and 10.	10-13
A	CN 111009683 A (BEIJING TAIFENG XIANXING NEW ENERGY TECHNOLOGY CO., LTD. et al.) 14 April 2020 (2020-04-14) See claim 3; paragraphs [0005], [0006], [0010], [0017], [0019], [0024] and [0038]; and example 1.	1-14

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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
* Special categories of cited documents:	
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Date of the actual completion of the international search	Date of mailing of the international search report
12 May 2022	12 May 2022

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/001751

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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5 **INTERNATIONAL SEARCH REPORT**
 Information on patent family members

International application No.

PCT/KR2022/001751

	Patent document cited in search report		Publication date (day/month/year)	Patent family member(s)		Publication date (day/month/year)
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				KR 10-1999-0085715 A		15 December 1999
20	KR	10-2019-0078770	A	05 July 2019	None	
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25	CN	111009683	A	14 April 2020	CN 111009683 B	23 November 2021
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REFERENCES CITED IN THE DESCRIPTION

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- KR 100412522 [0005]